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NRL Report 6510

Protective Coatings for Magnesium Alloys
Part 3 - Coordination Chemistry of the Magnesium Ion

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March 2, 1967

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ABSTRACT

Self-sealing protective coating systems for magnesium alloys must contain constituents which will react with corrosion products, or with the unprotected alloy itself, to form unreactive insoluble coatings. To develop such a protective system, a thorough knowledge of the coordination chemistry of the magnesium ion is needed. In this investigation, the coordination chemistry of magnesium ions was studied with respect to neutral, but polar, unidentate ligands in the presence of various donor anions. Complexes of the type $[\text{MgL}_n]\text{A}_2$ were prepared. Chemical analysis, infrared spectral data, and electrical conductivity were used to assign the structure of the isolated products. The ligands L were dimethyl sulfoxide, pyridine N-oxide, triphenylphosphine oxide, and triphenylarsine oxide. The value of n depended on the size of the ligand and the nature of the anion A, which was varied from a weak donor (perchlorate ion) to strong donors (acetate or methacrylate ions). The maximum value of n was six when the ligands were dimethyl sulfoxide or pyridine N-oxide and the anions were perchlorate ions. The bulkier ligands, triphenylphosphine oxide and triphenylarsine oxide, were sterically restricted to only four ligands per magnesium ion even when the anions were perchlorate ions. The methacrylate ions successfully competed for first coordination-sphere positions about the magnesium ions; the weak-donor ligands, dimethyl sulfoxide and pyridine N-oxide, were readily displaced. The infrared spectral data indicates that the methacrylate anions act as bidentate ligands; however, the stoichiometry of some of the complexes can only be explained if the acetate and methacrylate anions function as unidentate ligands. The results of this investigation suggest a study of polydentate ligands containing carboxyl groups as the active constituent in a self-sealing protective system for magnesium alloys.

PROBLEM STATUS

This is an interim report on the problem; work on the problem is continuing.

NRL Problem C04-04
Project RRMA 03-073/652-1/F020-03-01

Manuscript submitted November 9, 1966.

PROTECTIVE COATINGS FOR MAGNESIUM ALLOYS

PART 3 - COORDINATION CHEMISTRY OF THE MAGNESIUM ION

INTRODUCTION

Greatly improved protective coatings could extend the use of the light metal alloys, especially the more reactive magnesium, and reduce the amount of time required to maintain aircraft in proper operational condition. This Laboratory has begun the development of improved magnesium protective systems. The study involves three approaches: (a) the chemistry of magnesium and magnesium coordination compounds, (b) magnesium protective systems, and (c) techniques for the application or curing of protective coatings. Based on information from magnesium chemistry, formulations will be chosen to be tested in the other two approaches. Concurrent with the study of magnesium coordination chemistry, the application of coatings on alloys by thermal methods was also investigated (1,2).

The reactive nature of magnesium alloys, in a marine environment, requires that an ideal protective system for these alloys should exhibit self-sealing properties. Thus, if a breach occurs in the protective coating, the self-sealing coat could react to prevent extensive deterioration of the magnesium alloy. Two approaches to the development of a self-sealing protective coating are suggested: first, the applied coating or coatings could be of such characteristics that they would flow into the area of the breach and reseal the breach against attack by the marine atmosphere; second, the applied coating or coatings could contain constituents which would react at the site of the breach, with either corrosion products or alloy, to form a protective layer against further corrosion. Although the necessary flow characteristics of a coating of the first type to seal a breach would prevent its use on the outer surfaces of aircraft or missiles, its use in aircraft interiors would be practical. The second type of coating promises to be more useful as a general protective system for magnesium and is the type coating which will be investigated at this Laboratory.

Sack and Roe (3) have prepared an excellent literature survey of the corrosion of magnesium and magnesium alloys from 1940 to early 1956. The only reference to a self-sealing coating of the second type was a formulation containing selenates (4,5). The authors reported that if the protective film is breached, hydrogen selenide produced by decomposition of magnesium selenide deposited fresh selenium on the exposed metal. Shreider (6) reported that films of magnesium selenide were easily destroyed, leaving metallic selenium on the surface. Also, macrocouple which formed increased the corrosion rate. In an investigation by von Hippel and Bloom (7), the use of selenate coatings was examined as a substitute for chromate coatings. Although several patents for selenate protective systems have been reported (8,9), the toxicity and reduced paint adhesion on the coatings have not been conducive to widespread use. The investigation of other self-sealing systems has not yet been reported.

The necessary requirements for a successful self-sealing protective coating are (a) the coating must not react with the environment but must react at a breach in the coating, (b) the reaction at a coating-breach must produce a product that adheres to the alloy surface, (c) the coating must provide corrosion protection after self-sealing that is of the order of magnitude of the original coating, (d) the coating must be easily applied to the magnesium alloy without affecting the mechanical properties of the substrate, and (e) the new protective coating must be economical.

The approach taken by this Laboratory to provide a material satisfying the above requirements is the investigation of matrix systems containing organic ligands and inorganic or organic anions that could form insoluble coordination compounds with the magnesium-alloy oxidation products. Although unprotective magnesium alloys may be coated with insoluble magnesium salts such as hydroxide, carbonate, and sulfate, the easy removal of these magnesium compounds from the surface allows the marine atmosphere attack to continue. On the other hand, a properly chosen ligand, as well as anion, incorporated into a protective coating system and made available at the corrosion site could reseal a breach in the coating to prevent further corrosion. Obviously the ligands and anions would have to migrate to the exposed metal from the intact coating; such a migration would only be effective if the distances are relatively short. (How short remains to be determined.) The development of a ligand-anion system which satisfies the above requirements for a self-sealing coating necessitates an elucidation of the coordination chemistry of the magnesium ion.

The major research efforts in magnesium coordination chemistry have been directed toward analytical analyses, Grignard reagents, chlorophyll (a magnesium porphyrin), and magnesium elimination from hard waters. Water-insoluble coordination compounds of the type needed for magnesium protective coatings have not yet been reported. A review of the reported complexes of magnesium was undertaken to determine some of the general characteristics of magnesium coordination chemistry. Only a general summary of the conclusions noted in the literature survey will be considered pertinent to the present discussion. A few statements concerning the general properties of ligands will be considered first.

In general, the stability of complexes formed with small ionic ligands, with highly charged unidentate ligands, or with multidentate ligands, increases as the size of the metal ion decreases. For example, the sequence of stability for a given ligand is generally $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, where the ionic radii are 0.65, 0.99, 1.13, and 1.35 Å, respectively (10). Some magnesium complexes, however, are less stable than their calcium analogues. Although the relative instability of the ethylenediaminetetraacetic acid (EDTA) magnesium-complex appears to be due to an unfavorable heat change, which may reflect overcrowding or even failure of all the donor atoms of the multidentate ligand to engage with small cations, the relative instability of the formate and acetate complexes appears to be due to a small entropy change which may reflect outer-sphere complex formation (11). A ligand which will effectively coordinate with magnesium ions must be chosen to prevent weak outer-sphere complex formation and to utilize all of the available basic sites of the ligand when it coordinates with the cation.

The number of active basic sites and the structure of the ligand will be important factors in choosing a ligand system for a self-sealing protective system. Also of importance is the nature of the donor atoms on the ligand which form the bond between the basic site and the acid or acceptor magnesium ion. In general, donor atoms which give large ligand field splittings form their strongest complexes with metal ions which are particularly sensitive to ligand field stabilization. Donor atoms which produce small ligand fields tend to form relatively more stable complexes with metal ions which are insensitive to ligand field stabilization than for metal ions which are not. A more general summary of this statement was given by Ahrland, Chatt, and Davies (12) and extended by Pearson (13) to the concept of "hard" and "soft" acids and bases. Thus, magnesium ion, insensitive to ligand field stabilization or a "hard" Lewis acid, would prefer to bind strongly to "hard" nonpolarizable bases. Consistent with this concept, a consideration of the available data for stability constants of substituted iminodiacetates (14,15) indicates the relative donor atom stability sequences: oxygen > nitrogen > sulfur for the alkaline earth metal ions, but nitrogen > sulfur > oxygen for transitional metal ions with nearly filled *d* orbitals.

The affinity of magnesium ions for oxygen-containing ligands is also suggested by the preferential concentration of ^{18}O within the hydration sphere of Mg^{2+} (16). Thus, despite the ligand lability, there must be a substantial covalent contribution to the bonding between water of hydration and the central metal atom. Covalent contributions to the bonding exhibited by magnesium toward oxygen-containing compounds is also suggested by the coordination of ether molecules to Gignard reagents (R-Mg-X , where R is an organic group and X is a halogen).

The position of magnesium in the periodic table and the size and electronic configuration of the magnesium ion suggest that magnesium will coordinate with ligands through weak or labile bonds; however, ligands having oxygen as basic sites will be the most strongly bound. Since magnesium ions, in solution or in the solid state, exhibit a coordination number of six and an octahedral symmetry, a single polydentate ligand containing six oxygen coordination sites may be the best choice for maximum complex stability. Ligands, or a combination of ligands, with less than six basic sites may prove effective because of steric restrictions imposed by relatively large molecules surrounding the small magnesium ion.

The present study was undertaken to determine more fully the properties of solid magnesium coordination compounds, their ease of formation, and their stabilities. For this investigation, we chose to study relatively bulky, neutral, unidentate ligands which would exhibit weak donor properties similar to water, and which would coordinate with magnesium through oxygen atoms. Relatively bulky ligands sterically restrict the number of neutral ligands surrounding the magnesium ion; therefore, the systems studied should also provide coordination positions for relatively small negatively charged ligands (anions).

EXPERIMENTAL PROCEDURES

The neutral ligands investigated were dimethyl sulfoxide, pyridine N-oxide, triphenylphosphine oxide, and triphenylarsine oxide. The anions used to compete for coordination positions about magnesium were perchlorate ion, which exhibit weak tendencies to coordinate, and acetate and methacrylate ions, which exhibit a greatly increased tendency to coordinate with metal ions. The methacrylate ion was chosen also for its capability to polymerize to large polyanions.

Reagents

Commercial dimethyl sulfoxide, "Baker Analyzed" Reagent, was distilled under reduced pressure; the middle fraction collected at 42°C^* under a pressure of 3 torr was stored under dry nitrogen in a wash bottle which was sealed with rubber eyedropper bulbs. The reagent was conveniently dispensed by removing the rubber bulbs and applying dry nitrogen at the wash-bottle mouthpiece and collecting the dimethyl sulfoxide at the tip. The redistilled dimethyl sulfoxide had a measured specific conductance of $3.62 \times 10^{-7} \text{ ohm}^{-1}\text{-cm}^{-1}$ at 25°C ; the reported literature values are $3 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ (17), $3.6 \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$ (18), and $3 \times 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ (19).

Commercial pyridine N-oxide, Eastman Organic Chemicals practical grade, was distilled under dry nitrogen. The clear, colorless, middle fraction boiling between 106 and 107°C under a pressure of 2 torr was collected and stored under dry nitrogen in a stoppered flask, which was placed in a desiccator.

*All temperatures are uncorrected.

Triphenylphosphine oxide and triphenylarsine oxide were prepared by a modified procedure reported by Shriner and Wolf (20). Acetone solutions of triphenylphosphine or triphenylarsine were oxidized by 30% hydrogen peroxide. After the oxidation was completed, the acetone was removed by flash evaporation; the resulting white solids were then refluxed with dry benzene in an apparatus fitted with a Dean-Stark water trap to remove water from the preparation. Triphenylphosphine oxide (mp 158 to 159°C) or triphenylarsine oxide (mp 194 to 195°C) was isolated from the cooled benzene solutions. (Calculated for $C_{18}H_{15}PO$: P, 11.13%; found: P, 11.10%, 11.08%, and 11.33%. Calculated for $C_{18}H_{15}AsO$: As, 23.25%; found: As, 23.44% and 23.39%.)

Other Reagents

N,N-dimethyl formamide was redistilled before use, and the middle fraction which boiled at 48°C at a pressure of 15 torr was stored in a sealed wash bottle as described for the dimethyl sulfoxide. The specific conductance of the redistilled liquid was 2.3 to $4.8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C; the reported literature values range from 0.3 to $0.9 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ (21).

Reagent grade "anhydrous" magnesium perchlorate was used as received; however, analyses of the material were consistent with the formula $Mg(ClO_4)_2 \cdot 2H_2O$. (Calculated for $H_4O_{10}Cl_2Mg$: Mg, 9.38%; found: Mg, 9.06% and 9.16%.) Commercially available magnesium acetate was also used as received; analyses of the compound were consistent with the formula $Mg(CH_3CO_2)_2 \cdot 4H_2O$. (Calculated for $C_4H_{14}O_8Mg$: Mg, 11.33%; found: Mg, 11.38%.)

Magnesium methacrylate was prepared by reacting magnesium oxide or magnesium hydroxide with an equal mole ratio of glacial methacrylic acid in a small amount of water. The resulting solution was flash evaporated and the isolated white powder dried over Drierite in a vacuum desiccator. Magnesium analyses were consistent with the anhydrous salt. (Calculated for $C_8H_{10}O_4Mg$: Mg, 12.50%; found: Mg, 12.24%, average of six determinations.) Although there was a sharp color change from white to tan at a temperature of 255°C, the solid did not melt when heated to 300°C.

Absolute ethanol (USP Grade) was used as received without further purification.

Water used in the analyses and conductivity measurements was distilled and, before use, passed through a mixed-bed Penex M-8 resin (Penfield Mfg. Co., Inc.). The specific conductance of the demineralized distilled water was $2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ or less at 25°C; the reported literature value is $4 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 18°C (22).

Analyses

Ethylenediaminetetraacetic acid (EDTA) reagent was used to determine the magnesium content of the reported compounds. The procedure outlined by Reilley, Schmid, and Sadek (23) was used. In general, it was possible to add water to the solid sample, adjust the pH with an ammonia and ammonium chloride buffer, add Eriochrome Black T indicator, and titrate the sample with standard EDTA solution. For rapid titration, some of the insoluble samples required a concentrated nitric acid pretreatment prior to dilution and pH adjustment.

Since the magnesium analyses were generally in agreement with the proposed formula, total analyses on the coordination compounds were considered unnecessary. However, arsenic in the triphenylarsine oxide complexes was determined. The sample was digested in a mixture of concentrated sulfuric acid, nitric acid, and perchloric acid, reduced with hydrazinium sulfate according to the procedure of Smith and Fly (24), and

the final diluted solution of arsenic (III) was titrated with ceric sulfate solution (25). Dimethyl sulfoxide was determined by the method of Douglas (26).

Infrared Spectra

The infrared spectra of the coordination compounds in mineral oil mulls and potassium bromide pellets were recorded using a Perkin-Elmer Model 21 recording spectrophotometer.

Conductivities

The conductivities were measured using approximately 1×10^{-3} M solutions; N,N-dimethylformamide and demineralized distilled water were used as solvents. The conductances were determined in a three-piece dip-type electrode assembly (Fig. 1) as described by Crockford (27). The electrodes were conveniently cleaned by rinsing the assembly with reagent-grade acetone; a special outer jacket (Fig. 1a) with a gas inlet at the bottom was used to dry the assembly in a dry nitrogen stream for 15 to 20 minutes. After an acetone rinse, the outer jacket of the electrode assembly (Fig. 1c) was dried in an oven at 125°C and allowed to cool under dry nitrogen. The electrolytic conductivity of the solutions was measured with an Industrial Instruments, Inc., Model RC-16B Conductivity Bridge. Before measuring the resistance, the solutions were allowed to reach equilibrium in a $25 \pm 0.01^{\circ}\text{C}$ constant-temperature bath.

Preparation of Magnesium Coordination Compounds

The general method used to prepare the coordination compounds consisted of adding an ethanolic solution of the appropriate magnesium salt to an ethanolic solution of the desired ligand. Ten or 25 ml of ethanol was sufficient to dissolve the solids without warming. The mole ratio of ligand to magnesium salt was generally chosen so that the ligand concentration was always in excess. The ethanol-insoluble complexes were isolated by filtration, washed with ethanol, dried over calcium chloride in a vacuum desiccator, ground to a powder, and finally dried at 82°C in an Abderhalden apparatus under reduced pressure and over phosphorus (V) oxide. Several of the isolated products were extracted with warm benzene to insure complete removal of excess ligand. The benzene-extracted samples were dried in a vacuum desiccator over calcium chloride and paraffin wax prior to the final drying in the Abderhalden apparatus. Samples which appeared to decompose under the normal drying conditions were dried using a freeze-drying technique.

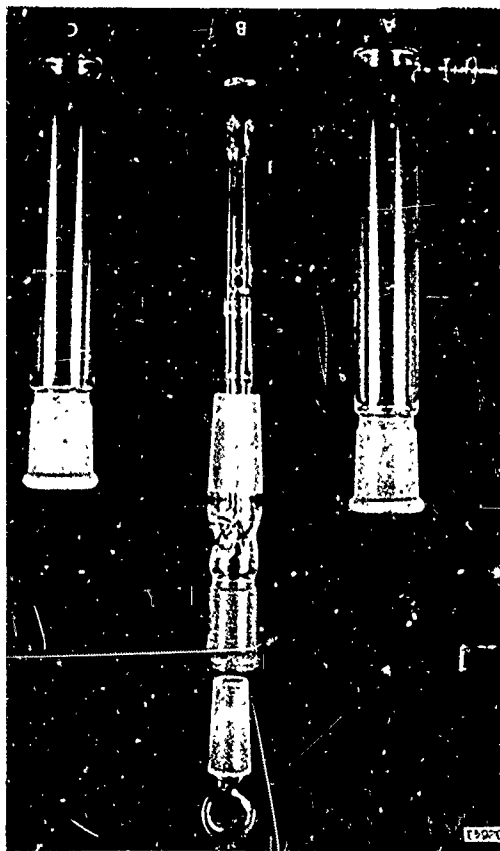


Fig. 1 - Three-piece dip-type electrode assembly used for conductance measurements: (a) drying jacket, (b) electrode assembly, and (c) outer jacket

If a precipitate did not form after mixing the ligand and magnesium salt, the resulting solution was flash evaporated until a slush was obtained. The solid was isolated by filtering, washing with ethanol, and drying as mentioned above.

A brief resume of pertinent observations for each ligand system follows.

Dimethyl Sulfoxide — The dimethyl sulfoxide complex (Table 1) was prepared by dissolving magnesium perchlorate in a large excess of the liquid ligand; the excess ligand was removed by flash evaporation and a final freeze drying. The isolated product was $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_2\text{H}_6\text{SO}$.

Pyridine N-Oxide

Reaction with Magnesium Perchlorate — After standing overnight in a stoppered flask, the reaction solution yielded the white precipitate $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{NO}$ (Table 2). The ethanol filtrate and wash solutions were flash evaporated and a white solid (found: 2.42% magnesium) was isolated, but not further identified.

Reaction with Magnesium Acetate — The reaction solution was stored for 1 week in a stoppered flask. Since no precipitate formed, the product was isolated when the ethanol was removed by flash evaporation. The hygroscopic residue was dried over phosphorus pentoxide under reduced pressures and at 80°C . Although some pyridine N-oxide sublimed from the product, a small amount of material was isolated which appeared to be the complex $\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{C}_5\text{H}_5\text{NO}$. The product isolated in a second preparation (Table 2, run b-2) was dried by the freeze-drying method at low temperatures, but the magnesium analyses were not consistent with the formula of any complex predicted.

Reaction with Magnesium Methacrylate — A white precipitate formed in the reaction solution during storage for 1 week in a stoppered flask. The insoluble material turned brown at 260°C but showed no melting to 300°C . The same complex was isolated when twice the quantities of reactants were used in the same volumes of ethanol (Table 2, run c-2). The analyses are consistent with the formula $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{NO}$. Pyridine N-oxide was isolated from the ethanol filtrate and wash solutions from both runs.

Table 1
Dimethyl Sulfoxide Complex

Ligand (L)		Salt (S)		Ratio L/S	Major Products	
Wt (g)	Milli- moles	Wt (g)	Milli- moles		mp (°C)	Analyses (% Found)
a. Magnesium Perchlorate <u>Mg(ClO₄)₂ · 2H₂O</u>				28/1	—	Mg: 3.52, 3.53, 3.24, 3.68, 3.76, 3.76 DMSO: 64.25, 65.80, 65.42, 66.13, 66.44, 65.88, 61.68, 68.80 [Mg(ClO ₄) ₂ · 6C ₂ H ₆ SO requires 3.51% Mg and 67.74% C ₂ H ₆ SO]
21.5	280	2.2	10			

Table 2
Pyridine N-oxide Complexes

Run	Ligand (L)		Salt (S)		Ratio L/S	Major Products	
	Wt (g)	Milli- moles	Wt (g)	Milli- moles		mp (°C)	Analyses (% Found)
a-1	a. Magnesium Perchlorate $[\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$				6.3/1	260-265	Mg: 3.20, 3.08, 3.08 [$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{NO}$ requires 3.06% Mg]
	1.20	12.6	0.45	2.0			
b-1	b. Magnesium Acetate $[\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}]$				9.7/1	—	Mg: 6.00, 5.77 [$\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{C}_5\text{H}_5\text{NO}$ requires 5.68% Mg]
	1.20	12.6	0.28	1.3			
b-2	1.20	12.6	0.28	1.3	9.7/1	—	Mg: 1.92, 1.95
c-1	c. Magnesium Methacrylate $[\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2]$				5.8/1	None to 300	Mg: 8.41, 8.39 [$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{NO}$ requires 8.40% Mg]
	0.61	6.42	0.21	1.1			
c-2	1.20	12.6	0.39	2.0	6.3/1	None to 300	Mg: 8.58, 8.54

Triphenylphosphine Oxide

Reaction with Magnesium Perchlorate — No precipitate formed when the magnesium perchlorate solution was added dropwise to the ligand solution. The residue, which was isolated after removing the ethanol by flash evaporation, did not melt over the temperature range to 300°C and was insoluble in cold water, partially soluble in benzene, and soluble in ethanol and acetone. The magnesium content found for the residue (1.54%, 1.53%) was not consistent with any reasonable formula. Since the solid appeared to be a mixture, the residue was extracted with cold benzene. Triphenylphosphine oxide was removed and the benzene-insoluble material was the magnesium complex $\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ (Table 3).

Reaction with Magnesium Acetate — Ethanol was removed from the reaction mixtures before products were isolated. The nature of the residue depended on the length of time the reaction mixture stood before flash evaporation and on the mole ratio of ligand to salt. For a 2-to-1 ligand-to-salt ratio, several days' storage (Table 3, run b-1) was necessary; no reaction occurred for shorter periods (runs b-2 and b-3) and only the reactants were isolated. The initial residue isolated from the reaction solutions appeared to be consistent with the formula $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO} \cdot \text{C}_2\text{H}_5\text{OH}$. (Calculated for $\text{C}_{42}\text{H}_{12}\text{O}_7\text{Mg}$: Mg, 3.26%; found: Mg, 3.21%, average of four determinations.) After treatment of this product with cold benzene, the benzene-insoluble $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ (Table 3) was filtered from the benzene solution and triphenylphosphine oxide was isolated from

Table 3
Triphenylphosphine Oxide Complexes

Run	Ligand (L)		Salt (S)		Ratio L/S	Major Products	
	Wt (g)	Milli- moles	Wt (g)	Milli- moles		mp (°C)	Analyses (% Found)
a-1	a. Magnesium Perchlorate $\text{Mg}(\text{ClO}_4) \cdot 2\text{H}_2\text{O}$				4/1	None to 300	Mg: 1.77, 1.75. P: 9.16, 9.18 [$\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ requires 1.82% Mg and 9.24% P]
	1.20	4.0	0.22	1.0			
b-1	b. Magnesium Acetate $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$				2/1	Indef.	Mg: 1.90, 2.08 [$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ requires 1.94% Mg]
	1.50	5.0	0.54	2.5			
b-2	1.50	5.0	0.54	2.5	2/1	—	No product isolated
b-3	1.50	5.0	0.54	2.5	2/1	—	No product isolated
b-4	3.0	10.0	0.54	2.5	4/1	Indef.	No analysis
c-1	c. Magnesium Methacrylate $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2$				2/1	Indef. to 210	Mg: 2.29, 2.38, 2.81, 2.33. P: 8.80, 8.68 [$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$ requires 2.36% Mg and 9.00% P]
	1.50	5.0	0.49	2.5			
c-2	1.50	5.0	0.49	2.5	2/1	Indef. to 210	Mg: 2.82, 2.73

the benzene solution. The complex softened at approximately 160°C; however, no melting was noted up to 300°C.

Increasing the mole ratio of ligand to salt (Table 3, run b-4) produced a benzene-insoluble material which was identical to the final complex isolated in run b-1. The benzene-insoluble complex was destroyed by extracting it with hot benzene in a soxhlet for 4 hours. Triphenylphosphine oxide was isolated from the benzene, and the benzene-insoluble material left in the extraction thimble was $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$. (Calculated for $\text{C}_4\text{H}_8\text{O}_5\text{Mg}$: Mg, 15.16%; found: Mg, 15.21%, average.)

Reaction with Magnesium Methacrylate — After standing several days in a stoppered flask, the reaction solution was flash evaporated. The pinkish glass isolated was dissolved in benzene, the unreacted $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2$ (calculated for $\text{C}_8\text{H}_{10}\text{O}_4\text{Mg}$: Mg, 12.50%; found: Mg, 12.55%) was removed by filtration, and the benzene removed by flash evaporation. The benzene-soluble material did not have a definite melting point; the solid softened between 145 and 152°C and then melted completely at 210°C. The melt turned

brown at higher temperatures. The analyses were consistent with the formula $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$ (Table 3).

Triphenylarsine Oxide

Reaction with Magnesium Perchlorate — An insoluble compound slowly formed when the ligand and salt solutions were mixed, however, the reaction solution was allowed to stand for three days before the solid $\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$ was isolated (Table 4). When the ethanol filtrate and wash solutions were flash evaporated, benzene-insoluble residues were isolated and analyzed. The residue found from run a-1, Table 4, was Mg, 2.74%, 2.81%; As, 11.36%. The residue found from run a-2 was Mg, 1.54%, 1.57%; As, 19.57%. These analyses were not consistent with the formulas of any predicted products.

Reaction with Magnesium Acetate — During a 2-week period, insoluble material slowly formed on the bottom of the stoppered flask used for run b-1, Table 4. This insoluble material contained only 0.31% arsenic, whereas the solid isolated after flash evaporation of the ethanol was $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$. When the complex was treated with cold benzene, triphenylarsine oxide was isolated from the benzene. (Calculated for $(\text{C}_6\text{H}_5)_3\text{AsO}$: As, 23.25%; found: As, 22.46, 22.89%; Mg, 0.02, 0.03%.) The benzene-insoluble product contained 12.01% magnesium (calculated for $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$: Mg, 11.34%).

When the ratio of ligand to salt was 2.2 to 1 (run b-2) no precipitate formed in the reaction solution after 1 week. The viscous residue which was isolated after the ethanol was removed was triturated with carbon tetrachloride. The carbon tetrachloride-insoluble product melted between 193 and 195°C, contained 21.70% arsenic, and its infrared spectrum was identical to that of triphenylarsine oxide (mp 194 to 195°C). The carbon tetrachloride insoluble solid did not analyze to a reasonable formula; the magnesium-to-arsenic ratio was found to be approximately 1 to 1.2.

Reaction with Magnesium Methacrylate — After standing 1 week (run c-2, Table 4) or 2 weeks (run c-1) no insoluble material formed in the reaction solution. Since the residue which was isolated from the ethanol in run c-1 did not give reasonable analyses, the solid was extracted with cold benzene. The benzene soluble material (found: Mg, 0.48%; As, 21.84% average) was impure triphenylarsine oxide. The benzene insoluble residue contained 12.53% magnesium. (Calculated for $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2$: Mg, 12.50%.) After the removal of ethanol from the reaction solution of run c-2, the viscous liquid residue was triturated with carbon tetrachloride; a pink polymer-like solid was isolated when the carbon tetrachloride was removed. The dried isolated material appeared to be $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ (Table 4).

Reaction with Magnesium Chromate — Because of the fineness of the brown solid, the insoluble material which formed in the yellow reaction solution was removed by centrifuging; however, no reasonable formula could be written from the analytical data. Ethanol-soluble material was identified as unreacted triphenylarsine oxide (mp 195°C; only traces of Mg).

RESULTS AND DISCUSSION

The stoichiometry of the isolated products is shown in Tables 1 through 4. For the relatively small ligands, such as dimethyl sulfoxide and pyridine N-oxide, a maximum coordination number of six is exhibited by magnesium ion when the anion of the compound is the weak-donor perchlorate ion. Only four bulkier ligands, such as triphenylarsine oxide and triphenylphosphine oxide, are able to surround the magnesium ion even in the presence of perchlorate ions. In the presence of the acetate and methacrylate anions, the neutral ligands apparently compete for inner-sphere coordination about the magnesium

Table 4
Triphenylarsine Oxide Complexes

Run	Ligand (L)		Salt (S)		Ratio L/S	Major Products	
	Wt (g)	Milli- moles	Wt (g)	Milli- moles		mp (°C)	Analyses (% Found)
<u>a. Magnesium Perchlorate</u> <u>[Mg(ClO₄)₂ · 2H₂O]</u>							
a-1	0.70	2.2	0.22	1.0	2.2/1	None to 300	Mg: 1.62, 1.61. As: 18.26, 18.40 (Mg: As = 1:3.67)
a-2	1.40	4.35	0.26	1.16	3.75/1	None to 300	Mg: 1.61, 1.61. As: 20.04, 20.06, 18.09, 19.68, 19.80 [Mg(ClO ₄) ₂ · 4(C ₆ H ₅) ₃ AsO requires 1.61% Mg and 19.81% As]
<u>b. Magnesium Acetate</u> <u>[Mg(C₂H₃O₂)₂ · 4H₂O]</u>							
b-1	1.40	4.35	0.28	1.3	3.35/1	—	Mg: 1.35, 1.35. As: 20.04, 19.94 [Mg(C ₂ H ₃ O ₂) ₂ · 4(C ₆ H ₅) ₃ AsO requires 1.70% Mg and 20.44% As]
b-2	0.70	2.2	0.22	1.0	2.2/1	130-160	Mg: 4.16, 4.19. As: 15.66, 15.67
<u>c. Magnesium Methacrylate</u> <u>[Mg(C₄H₅O₂)₂]</u>							
c-1	1.40	4.35	0.20	1.03	4.22/1	—	Mg: 1.29, 1.34 As: 19.96, 19.90
c-2	0.70	2.2	0.20	1.0	2.2/1	165-175	Mg: 2.44, 2.35, 2.31, 2.20 As: 17.61, 17.33 [Mg(C ₄ H ₅ O ₂) ₂ · 2(C ₆ H ₅) ₃ AsO requires 2.90% Mg and 17.87% As]
<u>d. Magnesium Chromate</u> <u>[MgCrO₄ · 7H₂O]</u>							
d-1	1.40	4.35	0.27	1.0	4.35/1	188 and resolid- ified	Mg: 4.74 As: 10.40 Cr: 14.79

ion. Depending on the donor strength of the anion and the donor strength and size of the neutral ligand, this competition will reduce the number of neutral ligands surrounding the magnesium ion. The tables show that in the series: perchlorate, acetate, and methacrylate ions, the number of a specific neutral ligand about the magnesium ion is smallest for the methacrylate anion. Thus, only one pyridine N-oxide, two triphenylarsine oxides, and three triphenylphosphine oxides are coordinated with magnesium in the presence of methacrylate ions.

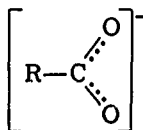
Magnesium methacrylate and magnesium complexes containing the methacrylate ion have low molar conductivities which are consistent with values for nonelectrolytes in dimethyl formamide (Table 5). The molar conductance of magnesium methacrylate in water indicates some dissociation of the salt, but not to the extent of a 2-to-1 electrolyte such as magnesium perchlorate in water. From the reported ranges of molar conductances (Table 6), it is seen that magnesium methacrylate dissociates to a 1-to-1 electrolyte in water. Because of the difficulty in preparing the acetate complexes, only the conductivity of the magnesium acetate complex containing triphenylphosphine oxide was determined. The conductivity of the tetrakis(triphenylphosphine oxide)magnesium acetate was consistent with the value for a nonelectrolytic in dimethyl formamide.

The weak donor, perchlorate anion, does not effectively compete for inner-sphere coordination positions about the magnesium ion. Ionization to 1-cation and 2-anions in solution was expected and was observed for complexes containing perchlorate ions. The low molecular conductivity of magnesium perchlorate 2-water in DMF (Table 5) may be explained by its higher concentration in DMF than the other compounds studied. However, further investigation of this observation is needed since the large increases of perchlorate concentration in water did not show the same lowering effect on the conductivity.

Although the identity of the magnesium chromate complex is not known, the low specific conductance and the relatively low melting point favor covalent bonding in the compound. This is in contrast with the magnesium perchlorate complexes which exhibit complete anion dissociation and do not melt up to 300°C.

The infrared frequencies associated with coordinated water are not definitive (28a). The wagging, twisting, and rocking modes are activated when water is coordinated to a metal; however, the frequencies, which may lie anywhere between 1000 and 650 cm^{-1} , are sensitive to the strength of the coordinate bond as well as to hydrogen bonding in the crystal. Reliance on the stretching modes is made difficult because of the C-H absorption in the region from 3550 to 3200 cm^{-1} , which is ascribed to antisymmetrical and symmetrical O-H stretching modes. Only the H-O-H bending mode, 1630 to 1600 cm^{-1} , can be used with confidence in the search for water participating in the coordination complexes. Although a very weak band in this infrared region was generally noted when potassium bromide pellets were used, the water is most likely caused by the handling of the materials without rigorous precautions to exclude moisture. Although $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ has a strong band at 1631 cm^{-1} , only a weak band in this region was noted for the $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2$. Because of the many broad bands in this region, due to the carbonyl absorption, no distinguishable bands could be found for the $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ attributable to water. Only the magnesium methacrylate complexes showed weak bands in the regions attributed to water; however, in all cases this may be due to handling procedures. Thus, the formulas reported were considered free from water in the first coordination sphere about the magnesium ion.

The usual coordination number of magnesium is six; however, the indication of lower apparent coordination numbers when methacrylate and acetate ions are present suggests that the nature of the bonding between magnesium and the carboxylic acid group RCO_2^- may be unidentate or bidentate (28b). Based on the infrared data obtained from various metal phenylstearates, Kagarise (29) postulated that the phenylstearate ion acts as a bidentate group



toward the metal ions which were studied.

Table 5
Molar Conductivities at 25°C for Magnesium Compounds Studied

Magnesium Compound	Mol. Wt.	Sample Wt. (g) in 50 ml of Solvent	Solvent	Conc. M ($\times 10^3$)	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$) $\text{L} \times 10^6$	Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2$) mole^{-1}	Mol. Cond. Avg. ($\text{ohm}^{-1} \text{cm}^2$) mole^{-1}
$\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	259.27	76.05	DMF	5.866	7.252	106.4	109
		76.05		5.866	7.543	110.7	
		70.35		5.427	6.842	108.6	
		70.35		5.427	7.016	111.3	
		28.25	H_2O	2.179	483.1	221.7	
		28.25		2.179	443.7	203.6	
		43.50		3.356	692.0	206.2	
		43.50		3.356	726.6	216.5	
		59.70		4.605	943.3	204.8	
		59.70		4.605	959.5	208.3	
		175.05		13.503	261.8	193.9	206
		175.05		13.503	266.3	197.2	
$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2$	194.5	8.70	DMF	0.895	4.417	4.9	5.0
		8.70		0.895	4.503	5.0	
		9.45		0.972	4.771	4.9	
		9.45		0.972	4.866	5.0	
		26.88	H_2O	2.764	358.4	129.8	131
		26.88		2.764	382.4	138.3	
		23.60		2.427	328.8	135.7	
		23.60		2.427	346.0	142.6	
		65.15		6.670	837.5	125.6	
		65.15		6.670	851.7	127.7	
		107.95		11.110	1368	123.2	156
		107.95		11.110	1398	125.9	
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{NO}$	793.8	36.10	DMF	0.884	137.7	150	
		36.10		0.884	149.4	163	
		37.70		0.950	145.0	153	
$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{NO}$	289.6	37.70	DMF	0.950	152.4	160	
		16.10		1.112	5.412	4.9	
		16.10		1.112	5.536	5.0	

Table 5 continues

of

Table 5 (Continued)

Magnesium Compound	Mol. Wt.	Sample Wt. (g) in 50 ml of Solvent	Solvent	Conc. M ($\times 10^3$)	Specific Conductance $\text{L} \times 10^6$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2$ mole $^{-1}$)	Mol. Cond. Avg. ($\text{ohm}^{-1} \text{cm}^2$ mole $^{-1}$)
$\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$	1336.4	13.80	DMF	0.953	5.036	5.3	5.1
		13.80		0.953	5.340	5.6	
		15.10		1.043	4.867	4.7	
		15.10		1.043	5.747	5.5	
		14.65		1.012	4.771	4.7	
$\text{Mg}(\text{CH}_3\text{CO})_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$	1255.6	14.65	DMF	1.012	5.028	5.0	151
		67.70		1.013	156.3	154.3	
		67.70		1.013	153.9	151.9	
		67.95		1.017	150.8	148.3	
		67.95		1.017	152.4	149.9	
$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$	1029.35	14.30	DMF	0.228	0.843	3.7	4.4
		14.30		0.228	1.138	5.0	
		50.75		0.986	0.4241	4.3	
		50.75		0.986	0.4373	4.4	
		51.55		1.000	0.4900	4.9	
$\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$	1512.2	51.55	DMF	1.000	0.5157	5.1	4.7
		79.65		1.053	152.7	144.9	
		79.65		1.053	169.5	160.8	
		79.50		1.051	157.6	150.0	
		79.50		1.051	163.1	155.0	
$\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$	838.2	75.75	DMF	1.002	153.0	152.7	155
		75.75		1.002	155.5	155.2	
		76.95		1.018	152.6	150.0	
		76.95		1.018	171.4	168.4	
		34.10		0.813	3.572	4.4	
Product from $\text{MgCrO}_4 + (\text{C}_6\text{H}_5)_3\text{AsO}$	—	34.10	DMF	0.813	3.679	4.5	4.4
		28.35		—	3.487	—	
		28.35		—	1.998	—	

Table 6
Reported Molar Conductance Ranges at Concentrations
of Approximately 10^{-3} M at 25°C

Charge Type	Number of Ions	Molar Conductivity ($\text{ohm}^{-1} \text{mole}^{-1} \text{cm}^2$)	
		Water Sol'n*	DMF Sol'n†
Nonelectrolyte	0	—	<10
1:1	2	96-115	50-85
2:1	3	225-270	140-170
3:1	4	380-432	200-260

*Mark M. Jones, "Elementary Coordination Chemistry," Englewood Cliffs, New Jersey:Prentice-Hall, 1964, page 254.

†G. Franz, J. Fujita, D. J. Phillips, J. V. Quagliano, S. Y. Tyree, Jr., and J. A. Walmsley, J. Am. Chem. Soc. 83:3770 (1961).

The internal modes of vibration of an ionized carboxyl group would be expected to be similar to the normal modes of a nonlinear XY_2 type molecule. As such, they consist of a symmetrical valence vibration (ν_1), an antisymmetrical valence mode (ν_2), and a vibration of deformation (ν_3). Duval, LeCompte, and Douville (30) have studied the infrared absorption spectra of more than a hundred salts of mono- or dibasic acids over the frequency range 600 to 1600 cm^{-1} . The approximate frequency ranges assigned to the three carboxyl-group vibrational modes are listed in Table 7 together with the values for the metal phenylstearates reported by Kagarise.

Table 7
Frequency Values Assigned to Carboxyl-Group Vibration Modes
and for Metal Phenylstearates

Metal	Vibration Mode Frequency (cm^{-1})		
	ν_1	ν_2	ν_3
Carboxyl (Ref. 30)	1350-1400	1550-1600	800-900
Li (Ref. 29)	1437	1587	935
Na (Ref. 29)	1441	1574	924
K (Ref. 29)	1412	1567	915
Ca (Ref. 29)	1439	1558	942

To study the three vibrational modes in the methacrylate ion, a series of metal methacrylates were prepared and their infrared spectra studied. The frequencies of interest are listed in Table 8 for comparison with those in Table 7.

The data shows that the ν_1 , ν_2 and ν_3 modes associated with the methacrylates are within the range reported by Duval et al. (30). In agreement with the data reported by Kagarise, the upper limit of the ν_3 mode should be 950 cm^{-1} instead of 900 cm^{-1} . A plot

Table 8
Frequencies Assigned to the Three Carboxyl-Group
Vibrational Modes for Metal Methacrylates

Metal Ion and Elec- tronegativities (Ref. 31)	Vibration Mode Frequency (cm ⁻¹)		
	ν_1	ν_2	ν_3
Mg ²⁺ 1.2	1418	1562	931
Na ⁺ 0.9	1412	1556	918
Mn ²⁺ 1.5	1414	1532	932
Zn ²⁺ 1.6	1418	1538	943
Cr ³⁺ 1.6	1422	1522	934
Fe ³⁺ 1.9	1418	1575	934
Cu ²⁺ 1.9	1410	1580	934

of the ν_2 values observed as a function of the electronegativities of the metal ions (31) is shown in Fig. 2

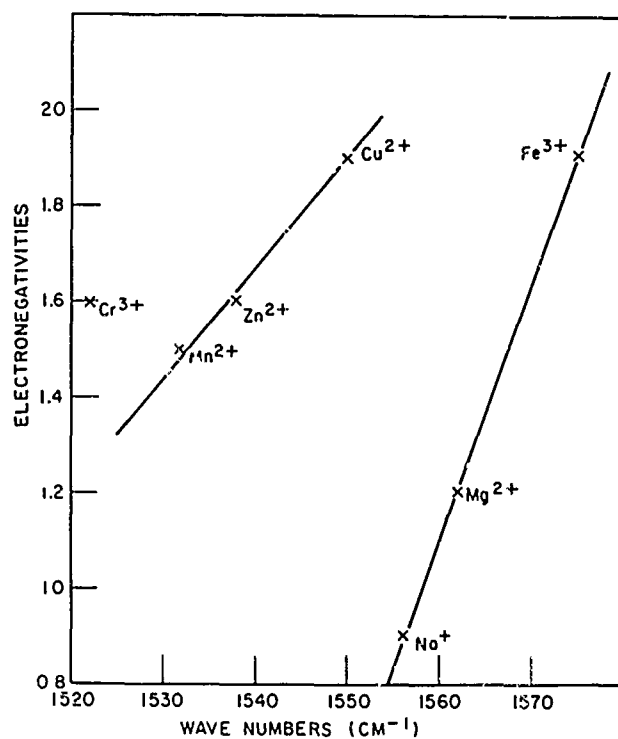
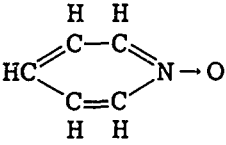
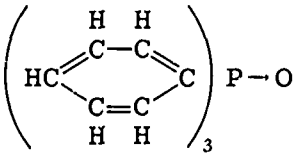
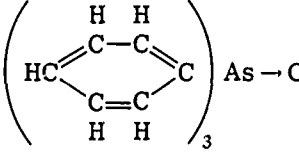


Fig. 2 - Relationship between electronegativities and antisymmetric C-O stretching (ν_2 vibration mode) of metal methacrylates

Two possible relationships are noted in Fig. 2: one relating the transitional elements Mn^{2+} , Zn^{2+} , Cu^{2+} , and the other relating the nontransitional elements Mg^{2+} and Na^+ and the transitional element iron (III). Infrared spectra of other metal methacrylates are being investigated to corroborate any distinct relationships and to study the anomalous chromium (III).

The infrared frequencies assigned to the three carboxyl-group modes of the magnesium methacrylate complexes (Table 9) indicate the same general ranges of frequencies as noted for the metal methacrylates and phenylstearates; however, a correlation between the ν_2 modes cannot be made. Certainly the type and number of ligands present about the magnesium ion will influence the observed frequency of the ν_2 mode. Although the triphenylphosphine oxide and triphenylarsine oxide complexes exhibit ν_2 modes at the same frequency, the ν_2 mode is shifted to higher frequencies when the less bulky pyridine N-oxide forms the magnesium complex.

Table 9
Frequencies Assigned to the Three Carboxyl-Group Vibrational Modes for Complexes of Magnesium Methacrylates

$\text{Mg}(\text{CH}_2=\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CO})_2 \cdot \eta \text{L}$		Vibration Mode Frequency (cm^{-1})		
η	Ligand L	ν_1	ν_2	ν_3
1		1418	1585	936
3		1420	1565	931
2		1420	1565	?

Assuming that the methacrylate ion is a bidentate ligand, the presence of only one pyridine N-oxide ligand in the magnesium methacrylate complex requires the unusual coordination number of five for magnesium. In this complex, the methacrylate ions may be in a higher field of magnesium electronegativity than present in the other two methacrylate complexes; consequently, the shift of the ν_2 mode to a higher frequency would be expected under these conditions. Although the complex $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$ also appears to have a magnesium ion of coordination number five, the complex may consist of one unidentate and one bidentate methacrylate ligand and three unidentate triphenylphosphine oxide ligands to satisfy a magnesium coordination number of six. The complex $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$, which appears to contain magnesium with a coordination number of four, could actually contain two bidentate methacrylate ions and two unidentate triphenylarsine oxide ligands to form a six-fold coordination. Triphenylphosphine oxide,

a stronger donor than the triphenylarsine oxide, may have displaced one bidentate negative ligand and forced it to act as a unidentate ligand. The fact that all three of the methacrylate complexes act as nonelectrolytes in dimethyl formamide (Table 5) indicates that the methacrylate ions are not readily displaced by the solvent.

Infrared spectra of magnesium acetate complexes did not show three carboxylic group vibrational modes as was found in methacrylate complexes. The apparent stoichiometry of the isolated acetate complexes indicates that the acetates are present as unidentate negative ligands. The infrared spectra of several hydrated-metal acetates were run, but no correlation of the carbonyl frequencies were noted. However, one point of interest was noted when magnesium acetate $[\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}]$ was dehydrated in the Aberderhalden drying apparatus over phosphorus (V) oxide. The ν_3 carbonyl mode which was present in the hydrated salt was absent in the dehydrated magnesium acetate (Table 10). The presence of the water ligands must influence the nature of the magnesium ion to acetate ion bonding. It is significant that the infrared spectra of the magnesium acetate complexes with the ligand systems studied showed none of the absorption bands for the bidentate carbonyl suggested by Kagarise for the phenylstearates (29) and observed in this investigation for the methacrylate complexes.

Since the symmetry of the free acetate ion (C_{2v}) is low, no marked differences in the spectrum would be expected for various structures of unidentate and bidentate bonding (32). The effect on the carbonyl frequencies, when the effective electronegativity of the metal is changed by altering the nature and number of the ligands, has little effect on the symmetrical and antisymmetrical CO stretching frequencies of the acetate complexes (Table 10). The two frequencies and their separations were close to that reported for free acetate ion (32).

Table 10
Observed Carbonyl Stretching Frequencies of Magnesium
Acetate and Magnesium Acetate Complexes

Magnesium Compound	C=O Stretching Frequencies (cm^{-1})			
	ν_3	ν_2 Anti-symmetric	ν_1 Symmetric	$\nu_2 - \nu_1$ Separation
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	943	1543	1408	135
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ (dehydrated)	—	1580	1428	152
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{C}_5\text{H}_5\text{NO}$	—	1590	1451	139
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$	—	—	—	—
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$	—	1587	1437	150
Free $[\text{CH}_3\text{COO}]^-$ (Ref. 32)	—	1578	1425	153

The group frequency shifts of the S—O, N—O, P—O, and As—O stretching frequencies have been extensively studied (33). In all cases transitional metals were investigated with the ligand systems, except for several acids and lithium (34). The infrared frequency shifts appear to be related to the electronegativity of the transitional metal ions and independent of the number of ligands present. The low electronegativity of Mg^{2+} , 1.2 (31), compared to most transition metals suggests only slight shifts, if any, in the observed S—O, N—O, P—O, and As—O stretching frequencies of the bonded ligands. Table 11 shows the observed group frequencies of the free ligand and the observed frequencies of the solid complexes.

Table 11
Observed Group Frequencies ν of the Free Ligand
and of the Ligand in Solid Complexes

a. <u>Pyridine N-Oxide (ν_{N-O})</u>		
1. Free ligand	1243 cm^{-1}	
2. $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{NO}$	1227	
3. $\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{C}_5\text{H}_5\text{NO}$	1237	
4. $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{NO}$	1230	
b. <u>Triphenylphosphine Oxide (ν_{P-O})</u>		
1. Free ligand	1185 cm^{-1}	
2. $\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$	1181	
3. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$	1189	
4. $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{PO}$	1188	
c. <u>Triphenylarsine Oxide (ν_{As-O})</u>		
1. Free ligand	881 cm^{-1}	
2. $\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$	894	
3. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$	879	
4. $\text{Mg}(\text{C}_4\text{H}_5\text{O}_2)_2 \cdot 3(\text{C}_6\text{H}_5)_3\text{AsO}$	881	
5. $\text{Mg CrO}_4 + (\text{C}_6\text{H}_5)_3\text{AsO} (?)$	887	
d. <u>Dimethyl Sulfoxide (ν_{S-O})</u>		<u>(ν_{S-C})</u>
1. Free ligand	1028 cm^{-1} (1055 neat)	699 cm^{-1} (694 neat)
2. $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{C}_2\text{H}_5\text{SO}$	<div><div>1053 } Mull</div><div>1026 }</div></div>	<div><div>1034 } KBr</div><div>1018 }</div><div>1002 }</div></div> <div>714</div>

The small differences noted in the N-O, P-O, As-O, or S-O stretching frequencies of the complexes compared to the free ligands indicate that there is little change in the bond order of the free ligands when they complex with magnesium. For the $\text{Mg}(\text{ClO}_4)_2 \cdot 4(\text{C}_6\text{H}_5)_3\text{AsO}$ complex, an unusual reduction in intensity and shift to shorter wavelengths of the ν_{As-O} cannot be explained at present. The four bulky triphenylarsine oxide ligands may be reacting through the less electronegative arsenic with the magnesium or perchlorate ions to cause the observed effect.

The dimethyl sulfoxide complex with magnesium perchlorate was the only solid which exhibited exchange when the material was examined in a potassium bromide pellet; the observed splitting of the perchlorate absorption and sulfur-oxygen stretching band supports the preliminary findings.

The perchlorate absorption in the 1140 to 1080 cm^{-1} region was generally observed to remain constant. The very intense absorption could not be used to observe possible shifting of the bands; however, all of the magnesium perchlorate complexes exhibited absorption in the designated region.

CONCLUSIONS AND FUTURE WORK

Complexes of magnesium perchlorate, magnesium acetate, and magnesium methacrylate with unidentate neutral, but polar, ligands were prepared. The complexes exhibited a maximum of six groups in the first sphere of coordination about the magnesium ion when the ligands were the relatively small dimethyl sulfoxide or pyridine N-oxide molecules. Only four of the more bulky ligands, triphenylphosphine oxide or triphenylarsine oxide, coordinated to the magnesium ion regardless of the anion.

The perchlorate and acetate ions did not compete successfully with the ligands for positions about the magnesium ion; however, the methacrylate ions did take positions normally occupied by the neutral ligands. The possibility of the methacrylate ions acting as a bidentate or as a unidentate ligand would explain why the stoichiometry of the (triphenylphosphine oxide or triphenylarsine oxide)magnesium methacrylate complexes appeared to be unusual. A study of the infrared spectra of various metal methacrylates and the magnesium methacrylate complexes indicated that the methacrylate ion can act as a bidentate ligand similar to phenylstearate (29). The strongest neutral donor investigated, triphenylphosphine oxide, apparently forced the methacrylate ion to also act as a unidentate negative ligand.

The conductivities of magnesium methacrylate complexes in dimethyl formamide support the conclusion that the methacrylate ions coordinate more strongly to magnesium than the other anion systems studied. For magnesium, the results of this study suggest a polycarboxylic acid or carboxyl-containing polydentate ligand to be incorporated into a self-sealing protective system. The additives migrating to magnesium ions formed by the corroding magnesium alloy could form an insoluble material, and the further eroding of the alloy would be prevented at a break in the original protective coating. The preparation of magnesium complexes containing polydentate ligands, or polymers containing carboxylate groups, and the investigation of the properties of the complexes are proposed. The nature of magnesium chromate complexes with various unidentate and polydentate ligands is also proposed to help elucidate the protective effect of chromate on magnesium materials.

ACKNOWLEDGMENTS

The author is indebted to E. B. Simmons, Jr., for technical assistance throughout this work, and to Dr. R. E. Kagarise for his assistance and suggestions in interpreting the infrared spectral data.

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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body, of abstract and index, annotation must be entered when the overall report is classified.

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Naval Research Laboratory Washington, D.C. 20390		Unclassified	
		2b. GROUP	
3. REPORT TITLE			
PROTECTIVE COATINGS FOR MAGNESIUM ALLOYS. PART 3 - COORDINATION CHEMISTRY OF THE MAGNESIUM ION			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
An interim report on the problem.			
5. AUTHOR(S) (First name, middle initial, last name)			
D.L. Venezky			
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS	
March 2, 1967	26	34	
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)		
NRL Problem C04-04	NRL Report 6510		
b. PROJECT NO.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
RRMA03-073/652-1/F020-03-01	None		
c.			
d.			
10. DISTRIBUTION STATEMENT			
Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
None		Dept. of the Navy (Naval Air Systems Command)	
13. ABSTRACT			
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DD FORM 1473 (PAGE 1)

S/N 0101-807-6801

23

Unclassified
Security Classification

<p>UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 6510. PROTECTIVE COATINGS FOR MAGNESIUM ALLOYS. PART 3 - COORDINATION CHEMISTRY OF THE MAGNESIUM ION, by D.L. Venezky. 26 pp. and figs., March 2, 1967.</p> <p>Self-sealing protective coating systems for magnesium alloys must contain constituents which will react with corrosion products, or with the unprotected alloy itself, to form unreactive insoluble coatings. To develop such a protective system, a thorough knowledge of the coordination chemistry of the magnesium ion is needed. In this investigation, the coordination chemistry of magnesium ions was studied with respect to neutral, but polar, unidentate ligands in the presence of various donor anions. Complexes of the type $[MgL_n]A_2$ were prepared. Chemical analysis, infrared spectral data, and electrical conductivity were used to assign the structure of the isolated products. The ligands L</p> <p>UNCLASSIFIED (over)</p>	<p>1. Magnesium alloys - Corrosion prevention</p> <p>2. Magnesium alloys - Coatings</p> <p>3. Magnesium ions - Chemical reactions</p> <p>4. Anticorrosive coatings - Materials</p> <p>5. Coordination compounds</p> <p>I. Venezky, D.L.</p>	<p>1. Magnesium alloys - Corrosion prevention</p> <p>2. Magnesium alloys - Coatings</p> <p>3. Magnesium ions - Chemical reactions</p> <p>4. Anticorrosive coatings - Materials</p> <p>5. Coordination compounds</p> <p>I. Venezky, D.L.</p>	<p>1. Magnesium alloys - Corrosion prevention</p> <p>2. Magnesium alloys - Coatings</p> <p>3. Magnesium ions - Chemical reactions</p> <p>4. Anticorrosive coatings - Materials</p> <p>5. Coordination compounds</p> <p>I. Venezky, D.L.</p>
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